



Chemical/morphological transition behavior of lithium phosphorus oxynitride solid-electrolyte in air: An analytical approach based on X-ray photoelectron spectroscopy and atomic force microscopy



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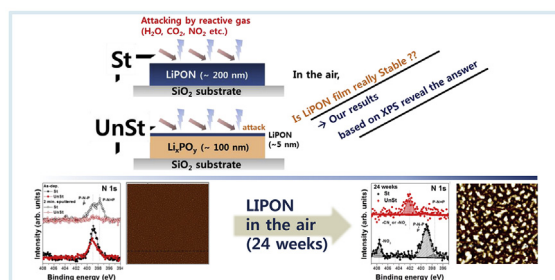
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HIGHLIGHTS

- The nitrogen composition effects on LiPON stability are clarified.
- The degradation mechanism of LiPON solid-electrolyte in air is illustrated.
- X-ray spectroscopy and atomic force microscopy explain well the degradation process.
- Graphene layer can slow down the aging process of LiPON solid-electrolyte.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Solid-electrolyte
Degradation mechanism
Lithium phosphorus oxynitride
Chemical stability
X-ray photoelectron spectroscopy
Atomic force microscopy

ABSTRACT

Lithium phosphorus oxynitride and lithium phosphate layers are prepared by controlling nitrogen composition using an optimized chemical vapor deposition process. Besides the predictable lithium phosphate layer decomposition process, progressive changes are observed in the lithium phosphorus oxynitride layer in air over time. These changes influence both the performance and stability of Lithium phosphorus oxynitride, utilized as solid-electrolytes or interface barriers in batteries. Therefore, to clarify the transition mechanism of them in air, a unique experiment is designed based on x-ray photoelectron spectroscopy. The results indicate that changes in the chemical structures of lithium phosphorus oxynitride and lithium phosphate occurred alongside morphological variations. Lithium phosphorus oxynitride layers undergo steady attacks by reactive gases in air, such as O₂, CO₂, and H₂O, resulting in an increased number of imperfect or dangling bonds and internal chemical reactions that in turn cause morphological changes. In addition, a graphene layer is employed to reduce the reactions of Lithium phosphorus oxynitride layers with reactive gases. The results show that the graphene-coated domains have relatively lower degradation rate than other regions. Overall, our results reveal the stability problems of lithium phosphorus oxynitride and lithium phosphate by demonstrating significant changes in the chemical/morphological structures exposed to air.

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1. Introduction

Electric products embedded with batteries are easily identified in all areas of modern life, from tiny stopwatches to sizable electric automobiles.^{1–2} The need for battery-related research is thus constantly growing for purposes such as device applications and parameter improvements in terms of performance, stability, safety, and cost [1–4]. Given the growing concerns regarding the industry-wide frequency of explosions and swelling in liquid-electrolyte-based batteries, solid-state electrolytes in the material optimization domain have become one of the hottest current research domains [3–5].

Lithium phosphorus oxynitride (LiPON) has been studied as a solid-electrolyte (SE) in Li-ion batteries due to its excellent conductivity ($> 10^6 \text{ Scm}^{-1}$), barrier effect against cathodes and Li metals, and material and electrochemical stability [6–12]. Conventionally, physical vapor deposition (PVD) processes such as sputtering, pulse lasers, and evaporation deposition are widely used for LiPON solid-electrolyte preparation; however, these are infeasible for real applications due to unavoidable limitations such as the non-uniformity of film depositions on three-dimensional substrates [13–16]. Most battery components, including cathode/anode electrodes and interlayers, have several micrometers of roughness and require large surface areas to optimize solid-electrolyte performance in battery cells [14–16]. None of the PLD processes listed above can fulfill these requirements [6,7,14,15]. Recently, the Rubloff and Karppinen groups have reported studies regarding a LiPON solid electrolyte atomic layer deposition (ALD) process, resulting not only in a homogeneous LiPON film prepared on various three-dimensional substrates, but also excellent film properties as a battery-cell solid-electrolyte [14–16].

In recent years, this research group has been working on a LiPON solid-electrolyte for application in batteries. Lithium phosphate (LiPO) and LiPON films were prepared using various deposition processes, and their film properties were characterized through proper analysis methods. It was discovered that all LiPO and LiPON films undergo varying degrees of obvious film property alterations when exposed to air. It is strongly believed these changes bring about performance degradation in battery cells [17,18]; however, few known studies discuss these transition behaviors. This study therefore designed a unique experiment based on X-ray photoelectron spectroscopy (XPS) to clarify the transition mechanism of LiPON (and LiPO) in air. Depending on nitrogen composition, two types of controlled LiPON films were prepared via chemical vapor deposition (CVD) and their chemical/morphological transitions in air were systematically characterized by various analyses. These results clearly elucidated the stability issues of LiPON solid-electrolyte exposed to reactive gases as an essential consideration for practical industry applications.

2. Materials and methods

LiPON and LiPO films were deposited on silicon (Si) substrates using the CVD process with the base reactor pressure controlled

at $< 10^{-2}$ Torr prior to deposition. Precursors of tert-butoxide (LiOtBu) (EG chem, 99.9%) and trimethylphosphate (TMP) (EG chem, 99.9%) were used with reactant N_2 gas to deposit LiPON films. Argon gas was used to inject and purge precursor materials and reactive gases during the deposition process. All precursors and reactant N_2 gas were simultaneously injected during the CVD process, and their injection ratios and deposition temperatures were controlled for process optimization. LiPO films were deposited without N_2 gas injection; however, the other experimental conditions remained equivalent to those of LiPON film deposition.

The LiPO film underwent various obvious film property changes as soon as it was exposed to air due to its explosive reactivity. To prevent this reaction, LiPO films were capped with a thin LiPON layer (approximately 5 nm thick). Based on air reactivity, LiPON films were named “St” and LiPO films capped with a thin LiPON layer were named as “UnSt”.

Both St and UnSt samples were stored in ambient air with a regulated relative humidity and temperature of $50 \pm 5\%$ and $22 \pm 2^\circ\text{C}$, respectively. The property variations of both over time were characterized using multiple analysis methodologies: chemical/electronic structures were investigated using X-ray photoemission spectroscopy (XPS, Quantera II) measurements including scanning photoelectron microscopy (SPEM, 8A1 beamline in Pohang Acceleration Laboratory); morphology and cross-section structures were characterized using a secondary emission microscope (SEM, JEOL JSM-7401F), optical microscopy (OM), and atomic force microscopy (AFM, Dimension); atomic compositions in the vertical direction were studied via secondary ion mass spectrometry (SIMS, TOF-SIMS) and XPS depth profiles; and ionic conductivity was calculated based on the electrochemical impedance spectroscopy (EIS) spectra.

In certain cases, Graphene (Gr) layers, grown by CVD process, were coated on both St and UnSt samples before being exposed to the air. Every Gr layer was transferred through dry transfer method [19]. This process allows of preventing LiPON films from being exposed to solvent, but unavoidably involves partial cracks in transferred graphene layer.

3. Results and discussion

As the deposition temperature of a LiPON film is one of the most critical factors affecting its properties [15,16,20], an in-depth study of the effects of deposition temperature on LiPON film properties was conducted after other experimental set-ups such as radio frequency (RF) power, substrate-distance from target source, and gas flow rates were completed [9–15]. Fig. S1 (a)–(e) and S2 (a)–(b) involve the comparative experimental results of LiPON film properties after deposition at temperatures ranging between 200 and 375°C . LiPON films must meet several requirements before use as solid-electrolyte layers, including high N concentration, homogeneous crystal structure, uniform morphology, and excellent ionic conductivity [15–17,20,21]. The film properties in Figs. S1 and S2 easily established the optimum

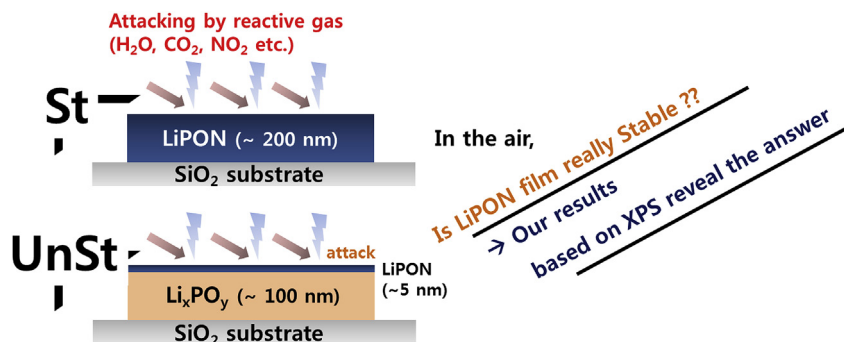


Fig. 1. Schematic diagram briefly describing LiPON (and LiPO) sample information and the aims of this study.

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